Water-like Anomalies and Breakdown of the Rosenfeld Excess Entropy Scaling Relations for the Core-Softened Systems: Dependence on the Trajectory in Density-Temperature Plane

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We show that the existence of the water-like anomalies in kinetic coefficients in the core-softened systems depends on the trajectory in $\rho - T$ plane along which the kinetic coefficients are calculated. In particular, it is shown that the diffusion anomaly does exist along the isotherms, but disappears along the isochores. We analyze the applicability of the Rosenfeld entropy scaling relations to the systems with the core-softened potentials demonstrating the water-like anomalies. It is shown that the validity of the of Rosenfeld scaling relation for the diffusion coefficient also depends on the trajectory in the $\rho - T$ plane along which the kinetic coefficients and the excess entropy are calculated. In particular, it is valid along isochors, but it breaks down along isotherms.

It is well known that some liquids (for example, water, silica, silicon, carbon, and phosphorus) show an anomalous behavior [1–6]:their phase diagrams have regions where a thermal expansion coefficient is negative (density anomaly), self-diffusivity increases upon compression (diffusion anomaly), and the structural order of the system decreases with increasing pressure (structural anomaly) [3, 4]. A number of studies demonstrate water-like anomalies in fluids that interact through spherically symmetric potentials (see, for example, [7, 12, 25] and references therein).

It was shown [5, 6] that thermodynamic and kinetic anomalies may be linked through the excess entropy. In particular, in Refs. [5, 6] the authors propose that the entropy scaling relations developed by Rosenfeld can be used to describe the diffusivity anomaly.

In 1977 Rosenfeld proposed the relations connecting transport properties of a liquid with the excess entropy [8]. In order to write down these relations one should use the reduced forms of the transport coefficients:

$$D^* = D\frac{\rho^{1/3}}{(k_B T/m)^{1/2}}, \tag{1}$$

where D is the diffusion coefficient. According to the Rosenfeld suggestion, the reduced diffusion can be expressed in the form

$$D^* = a \cdot e^{bS_{ex}}, \tag{2}$$

where $S_{ex} = (S - S_{id})/(Nk_B)$ is excess entropy of the liquid and a and b are the constants which depend on the studying property [9]. The coefficients a and b show an extremely weak dependence on the material and can be considered as universal.

In his original works Rosenfeld considered hard spheres, soft spheres, Lennard-Jones system and one-component plasma [8, 9]. After that the excess entropy scaling was applied to many different systems including core-softened liquids [5, 6, 10–12], liquid metals [13, 14], binary mixtures [15, 16], ionic liquids [17, 18], network-forming liquids [10, 17], water [19], chain fluids [20] and bounded potentials [12, 21, 22].

Nevertheless, controversies still remain. For example, up to the moment it is not clear whether the Rosenfeld scaling relations are applicable to the core softened systems. Some publications state that the scaling relations are valid for such systems [6, 11], while in our recent work it was shown that the scaling relations may break down for the core softened systems [12]. This article presents a discussion of this contradiction. Basing on the molecular dynamics simulations of the two core-softened systems we show that the existence of the water-like anomalies and the validity of the Rosenfeld scaling relations depend on the trajectory in the $(\rho-T)$ plane, along which the kinetic coefficients are calculated. For the first time it is explicitly shown that the water-like anomalies in the systems with core-softened potentials do exists when the kinetic coefficients are calculated along the isotherms and do not exist along the isochores. Consequently, the exponential functional form of the relation between the excess entropy and the reduced diffusion coefficient holds along isochors while along isotherms one observes its breakdown.

Two systems are studied in the present work. The first one is a repulsive shoulder system (RSS) introduced in our previous works [24, 25]. This system has a potential

$$U(r) = \left(\frac{\sigma}{r}\right)^{14} + \frac{1}{2}\varepsilon \cdot [1 - \tanh(k_0\{r - \sigma_1\})], \tag{3}$$

where σ is the "hard"-core diameter, $\sigma_1 = 1.35$ is the soft-core diameter, and $k_0 = 10.0$. In Ref. [25] it was shown that this system demonstrates anomalous thermodynamic behavior. In our previous publication [12] the Rosenfeld relation for this system was studied. It was shown that the scaling relation for the diffusion coefficient breaks down for this system in the anomalous diffusion region along the isotherms.

The second system studied in this work is the core-softened system introduced by de Oliveira et al [23]. This system is described by the spherically symmetric potential represented by a sum of a Lennard-Jones contribution and a Gaussian-core interaction (LJG):

$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] + a\varepsilon \cdot \exp \left[-\frac{1}{c^2} \left(\frac{r - r_0}{\sigma} \right)^2 \right], \quad (4)$$

with $a = 5.0$, $r_0/\sigma = 0.7$ and $c = 1.0$. This model can qualitatively reproduce water's density, diffusivity, and structural anomalies. The diffusivity of this system was studied, for example, in the papers [11, 23].

In this paper we use the dimensionless quantities: $\tilde{\mathbf{r}} = \mathbf{r}/\sigma$, $\tilde{P} = P\sigma^3/\varepsilon$, $\tilde{V} = V/N\sigma^3 = 1/\tilde{\rho}$, $\tilde{T} = k_B T/\varepsilon$. Since we use only these reduced units we omit the tilde marks.

The simulation setup of the RSS was described in detail in Ref. [12]. The following isotherms are simulated: $T = 0.2; 0.25; 0.3; 0.35; 0.4; 0.5; 0.6; 0.7$ and 0.8.

For the investigation of the LJG potential we simulate a system of 1000 particles in a cubic box for the densities ranging from $\rho = 0.01$ till $\rho = 0.35$ with the step $\delta\rho = 0.01$. The time step used is $dt = 0.001$. The equilibration period consists of $1 \cdot 10^6$ time steps and the production period - $2.5 \cdot 10^6$ time steps. During the equilibration the temperature is kept constant by velocity rescaling while during the production cycle NVE-MD is used. The equations of motion are integrated by velocity-Verlet algorithm. The following isotherms are simulated: $T = 0.2; 0.3; 0.4; 0.5; 0.6; 1.0$ and 1.5.

The excess entropy in both cases was computed via thermodynamic integration method. For doing this we calculate excess free energy by integrating the equation of state along an isotherm: $\frac{F_{ex}}{Nk_BT} = \frac{F - F_{id}}{Nk_BT} = \frac{1}{k_BT} \int_0^\rho \frac{P(\rho') - \rho' k_B T}{\rho'^2} d\rho'$. The excess entropy is computed via $S_{ex} = \frac{U - F_{ex}}{Nk_BT}$.

Fig. 1(a) presents the diffusion coefficient of the RSS system as a function of ρ and T. Fig. 1(b) demonstrates the excess entropy as a function of ρ and T. From these figures it follows that the diffusion coefficient and the excess entropy along an isotherm have similar qualitative behavior. From Figs. 1(a) one can see that there is a diffusion anomaly along the isotherms, but there is no anomaly along the isochores. Moreover, it is possible to find the trajectories in the $(\rho - T)$ plane, along which the diffusion anomaly does not exist. For example, it may be shown that there is no diffusion anomaly along the isobars. This issue will be discussed in detail in the subsequent publication.

In our previous publication [12] we showed that for this system the Rosenfeld scaling relation along isotherms is not applicable: the curves demonstrate the self crossing loops (see Fig. 2 (b)). Fig. 2 (a) represents the logarithm of the reduced diffusion coefficient along a set of isochors for the RSS. As it can be seen from this figure, the depen-
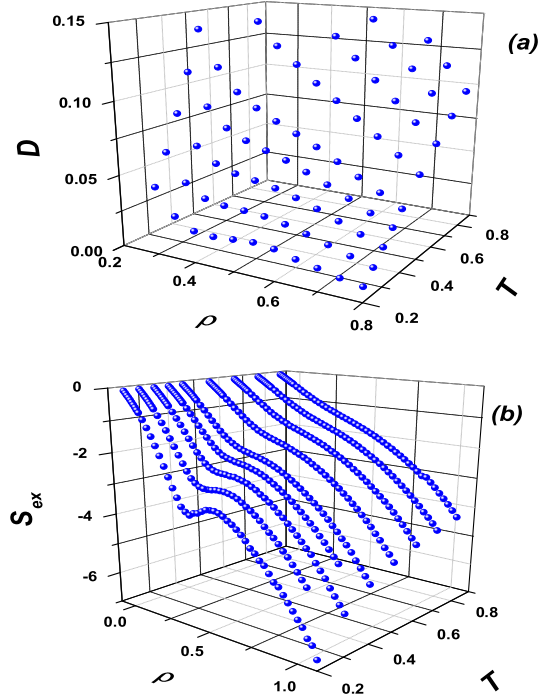

FIG. 1: (Color online) (a) The diffusion coefficient of the RSS system as a function of ρ and T. (b) The excess entropy of the RSS system as a function of ρ and T.

dence of D^* on S_{ex} is linear. However, the slope of the line shows an isochor dependence. Fig. 2 (a) shows that the slope remains approximately constant for low densities ($\rho = 0.3 - 0.55$) while on increasing the density the slope also increases. From Figs. 2 ((a) and (b)) one can conclude that the Rosenfeld scaling relation hold along the isochores, but breaks down along the isotherms.

In order to show that the dependence of the water-like anomalies and the Rosenfeld scaling relations on the trajectory in the $(\rho - T)$ plane is a general property of the core-softened systems we study another core softened potential introduced above - the LJG potential. Fig. 3(a) presents the diffusion coefficient of the LJG system as a function of ρ and T. As in the case of RSS, one can see that at low temperatures there is the diffusion anomaly. Fig. 3(b) demonstrates the excess entropy as a function of ρ and T. From Figs. 3((a) and (b)) one can see that there is a diffusion anomaly along the isotherms, but there is no anomaly along the isochores (compare Figs. 1 ((a) and (b)). From these figures it follows that the diffusion coefficient and the excess entropy along the isotherms have similar qualitative behavior. However, the location of the extremum points of diffusivity and excess entropy along the isotherms is different (Fig. 4). It means that there are some regions where one function increases while another one decreases and vice versa. Clearly, this kind of behavior can not be consistent with the Rosenfeld scaling formula. From this one can conclude that the Rosenfeld
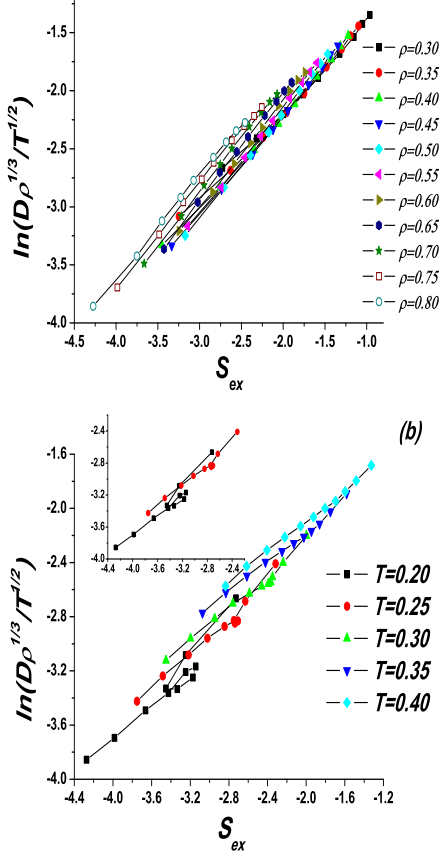
FIG. 2: (Color online). (a) Reduced diffusion logarithm for RSS along a set of isochors. (b) The logarithm of the reduced diffusion coefficient as a function of S_{ex} along a set of isotherms for RSS.

scaling relation is not applicable to the diffusivity along an isotherm for the LJG model. It should be noted that the behavior depicted here is consistent with simulation results for other water-like fluids (see, for example Ref. 5) therefore one can expect that the violation of the Rosenfeld scaling relation along the isotherms is the general feature for the systems with the water-like anomalies.

Fig. 5 (a) presents the logarithm of reduced diffusion coefficient versus excess entropy along a set of isotherms. One can see that at low temperatures the curves demonstrate the selfcrossing loops like the ones observed for the RSS model (see Ref. [12] anf Fig. 2 (b)). These loops become less pronounced with increasing the temperature and at $T = 0.5$ the self crossing disappears.

It can be seen from Figs. 3((a) and (b)), that both the diffusivity and the excess entropy along isochors are monotonous. It allows to expect that, as in the case of RSS, the exponential relation between the diffusion coefficient and the excess entropy holds along isochors. Fig. 5 (b) shows the $\ln(D^*)$ versus S_{ex} along a set of isochors. From this figure one can see that all curves with good ac-
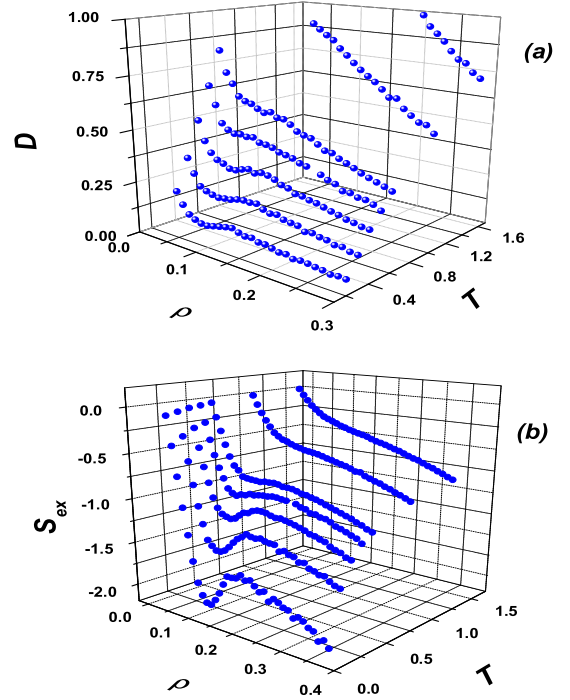

FIG. 3: (Color online). (a) The diffusion coefficient of the LJG system as a function of ρ and T. (b) The excess entropy of the LJG system as a function of ρ and T.
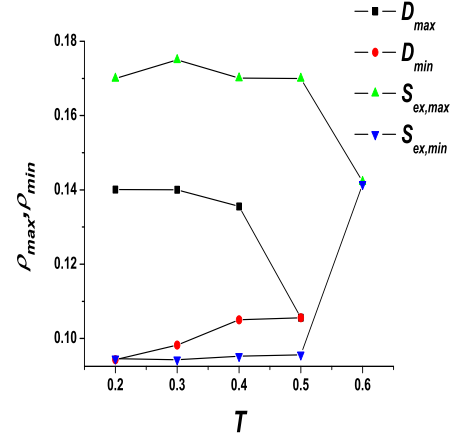

FIG. 4: The densities of maximum and minimum of the diffusivity and the excess entropy for the several isotherms.

curacy correspond to the Rosenfeld scaling relation. This result is in agreement with Refs. [6, 11]. However, Fig. 5 (a) contradicts to the Refs. [6, 11]. For example, in Fig. 3 of Ref. [11] the authors present the anomalous behavior of the diffusion coefficient along the isotherms, but show the Rosenfeld relation along the isochores and make the wrong conclusion that the Rosenfeld-type excess entropy scaling is valid for the LJG system.

In conclusion, in the present article we carry out a molecular dynamics study of the two core-softened sys-
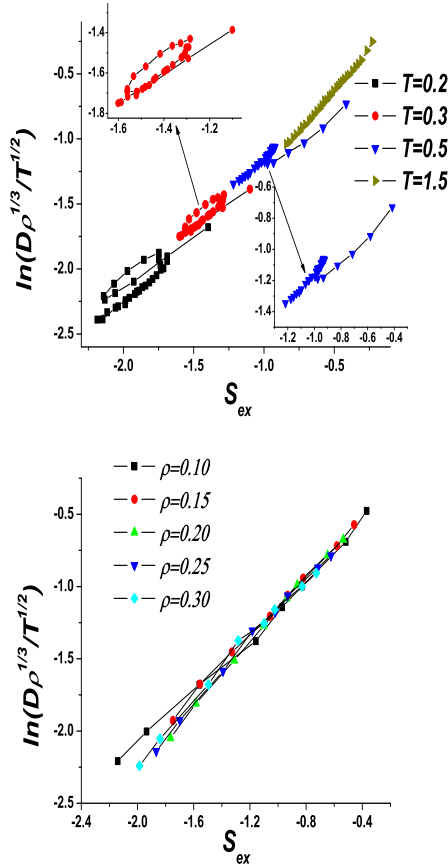
FIG. 5: (Color online). (a) The logarithm of the reduced diffusion coefficient for the LJG model along the several isotherms. The insets correspond to the temperatures $T = 0.3$ (upper panel) and $T = 0.5$ (lower panel) in the larger scale. (b) The logarithm of the reduced diffusion coefficient for the LJG model along the several isochors.

tems (RSS and LJG) and show that the existence of the water-like anomalies in kinetic coefficients in these systems depends on the trajectory in $\rho - T$ plane along which the kinetic coefficients are calculated. In particular, it is shown that the diffusion anomaly does exist along the isotherms, but disappears along the isochores and isobars. We analyze the applicability of the Rosenfeld entropy scaling relations to these systems in the regions with the water-like anomalies. It is shown that the validity of the of Rosenfeld scaling relation for the diffusion coefficient also depends on the trajectory in the $\rho - T$ plane along which the kinetic coefficients and the excess entropy are calculated. In particular, it is valid along isochors, but it breaks down along isotherms.

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